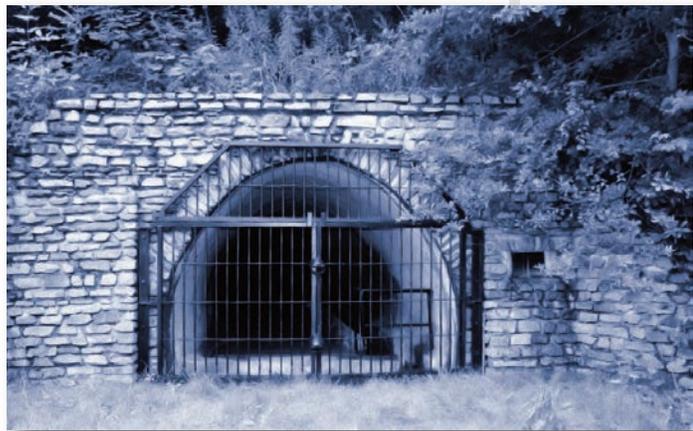


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Performance Boundaries of a Passive Biological Water Treatment System for Arsenic and Radium Immobilisation from Flooded Uranium Mines

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Abstract Due to concerns with biological treatment efficiencies during uranium mine water remediation, fundamental processes governing arsenic and radium immobilization were examined in a pilot-scale constructed wetland over a period of three years. Water, biological and sediment samples were collected regularly for investigation using, inter alia, biomaterial and crystallography methods and complimentary laboratory experiments to gain insight into specific processes. The results reveal the existence of a competing abiotic and biotic processes which limit the efficiency of the constructed wetland. Sorption, precipitation and co-precipitation are the principal As-immobilization processes, which are antagonized by biological processes.

Keywords constructed wetland, biomaterial, remediation

Introduction

Recent studies have demonstrated many pilot-scale constructed wetlands fail to achieve anticipated remediation expectations, especially with respect to removal of toxic metals and metalloids from abandoned mine water (Hallberg and Johnson 2003; Keiper *et al.* 2002; La Force *et al.* 2000; Woulds and Ngwenya 2004). Poor remediation performance of many constructed wetlands is consistent with findings of high rates of remobilization of metals and metalloids within most bench-scale studies and natural wetlands (Marchand *et al.* 2011). A number of reasons have been postulated, with Dudel *et al.* (2004) suggesting a lack of consideration of holistic ecosystem functions in the design of essentially monoculture-constructed wetlands being one of the major problems. While true, contemporary literature reports few constructed wetlands capable of successfully treating acid mine drainage (AMD). Thus, there are multiple factors contributing to poor performance in addition to ecologically-insensitive design. Consequently, a study was designed to investigate, using biomaterial and crystallographic procedures, the ecological

processes modifying arsenic and radium dynamics within a pilot-scale constructed wetland-treating water from flooded shafts of an abandoned uranium mine.

Methods

Study site – pilot-scale constructed wetland

The study took three years and was conducted at a pilot-scale constructed wetland in western Ore Mountain (Erzgebirge) in the Free State of Saxon, Germany. The constructed wetland was a pilot-scale facility for passive treatment of shaft floodwaters draining from an abandoned uranium mine. The wetland consisted of two parallel channels ("Becken" A and B), each of four serial reaction cells (aka ponds B 1, B 2, B 3, and B 4) and a pre-aeration cascade. The pilot plant was predominantly planted with the macrophytic algae Characeae vulgaris.

Sediment investigations

Sediment was collected from the "Becken" A series only, where sediment traps were placed at the inlets and outlets of ponds 2 to 4 (coded B 2A-1 to B 4A-1 for inlets and B 2a-2 to B 4a-2 for outlets) and collected sediments were sequen-

tially extracted and used in the current procedures.

Water sampling

Water was sampled regularly throughout the three years of the study. Immediately after collection, samples were filtered through a pre-cleaned 1.2 µm pore glass-fibre filter into pre-washed containers. Filtered water samples were transported to the laboratory for arsenic fractionation to different sizes using ultrafiltration. At least 5 L of pre-filtered mine water samples were ultra-filtered on a 0.2 µm membrane within 24 h of collection. The ultrafiltration was conducted at high pressure with ultrafiltration membranes with molecular weight cut-offs of 450 nm, 200 nm, 25 nm, 10 nm, and 1–3 nm. The ultrafiltration procedure used in the current study was modified from Eyrolle and Charmasson (2001) and Guo *et al.* (2007). Samples were handled according to DIN standards for heavy metal-contaminated water.

Analysis

Particulates filtered from water samples on 1.2 µm, 0.45 µm and 0.2 µm filters were analysed for organic carbon, metals and uranium. The samples were then analysed for multiple elements using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS ELEMENTAL PQ2 VG +, London, England). Total and dissolved organic carbon (TOC and DOC) in the water samples were determined with FORMACS HT TOC/TN Analyser (Scalar, Breda, the Netherlands) according to DIN EN 1484 (1997). Scanning Electron Microscopy coupled with EDX (SEM Carl Zeiss, Jena) function was used to characterise the colloid population on the particulates re-

tained on the filter membranes. Radium activity was determined using gamma spectroscopy and crystals were analysed using X-ray Diffractometry. All reagents were of analytical grade (Suprapur, Merck GmbH Darmstadt, Germany).

Results and methods

Physical-chemical properties of water

To ensure representative samples, selected physicochemical parameters of the water were measured during each field sampling. The Eh, pH, conductivity, temperature, iron and dissolved oxygen concentrations recorded in the tailing ponds are presented in Table 1. The quantity of mobile particulate material present were strongly dependent on water properties, including pH, ionic strength, and anion concentrations. Maximum particulate release occurred under low ionic strength and alkaline water conditions. In general, the particulate matter concentrations decreased with increasing conductivity. Therefore, high pH and low conductivity conditions in mine water promote the formation of waterborne particulates in all treatment ponds.

Arsenic transport in water

Water analysis revealed concentrations in inflow and outlet waters (respectively) of manganese (2.7 and 2.0 mg L⁻¹); uranium (0.97 and 0.5 mg L⁻¹); radium (4.4 and 1.1 Bq L⁻¹); arsenic (3.2 and 0.45 mg L⁻¹); and iron (36 and 1.8 mg L⁻¹). Thus, the treatment wetland failed to reduce both arsenic and radium activity below directive values of 0.02 mg L⁻¹ and 0.4 Bq L⁻¹, respectively. Further, fluctuations in As concentrations resulted in output concentrations from treatment cells exceeding input

Parameter	Units	Becken 2A			Becken 3A		Becken 4A	
		Inlet	Middle	Outlet	Inlet	B3A-2	Inlet	Outlet
pH		7.0	7.1	7.1	7.4	7.5	7.7	7.6
Redox	mV	377.0	379.0	379.0	349.0	356.0	346.0	349.0
Conductivity	mS/cm	0.5	0.5	0.5	0.4	0.5	0.4	0.4
Dissolved Oxygen	mg/L	0.8	0.4	2.8	2.0	2.3	2.2	3.6
Temperature	°C	26.3	24.6	24.4	26.8	26.4	26.4	25.1

Table 1 The physical-chemical properties of the water

values during some periods of the year, calling in to question the long-term sequestration of these contaminants. The form of As transport in the water was determined by differentiating the total arsenic content after filtration on 0.2 μm pore and after ultrafiltration at 30 kD (Fig. 2), indicating most As is transported as particulate matter. A trial to fractionate radium proved futile due to problems determining radium using spectroscopic methods.

Arsenic and radium in sediments

Fig. 3 illustrates the total arsenic and iron in sediments from collected from the sediment traps. Fractionation revealed that the majority of the arsenic is deposited in the sediments both in amorphous form as well as bound to crystalline Fe compounds (data not shown). Reducible arsenic species, likely as arsenate due to this forms higher adsorption capacity to iron compounds and organic colloids, dominant the profile, followed by bound arsenic species. This confirms the binding of arsenic in amorphous and crystalline Fe compounds is an important mechanism of arsenic sequestration in immobilization mine water. Crystalline Fe compounds are likely ionic as X-ray

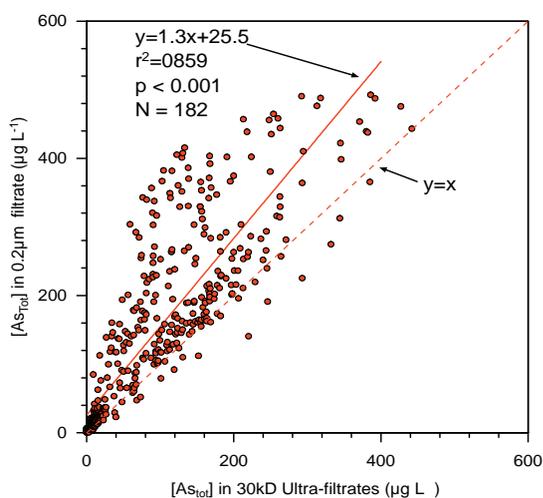


Fig. 2 The ratio between total dissolved and particulate arsenic after filtration on 0.2 μm to ultrafiltration 30 kD. The data is from water samples collected from all treatment ponds

diffraction found no Fe mineral phases in the sediments (data not shown). Sediment partition studies suggested arsenic immobilization was predominantly abiotic through either adsorption or co-precipitation with Mn and Fe as the organic partition was negligible.

Unlike arsenic, it was difficult to determine if most radium was bound to organic compartments within the sediments. Elution studies revealed that most radium, which was strongly bound to the sediments could not be easily remobilised (Fig. 4). This observation supported the results of the study that the uptake of radium by Characea was the main mechanism of radium removal in constructed wetland. Indeed, Characea biomass analysis revealed very high radium bioactivity of 33.1 kBq kg⁻¹.

A few reports have attributed the high radium uptake by Characea to its calcareous surface (REFERENCE). SEM-EDX analysis (Fig. 5 a and b) compliment X-ray diffraction procedure (data not shown) proved the high degree of calcification on the surface of Characea.

Neither Ra nor Ba-species were found on the surface of Characea. To evaluate if radium was complexed to the calcite on the surface of the Characea, the calcite was extracted. However, extraction of surface calcite did not reduce radium content in the biomass (Table 2) indicating most of the radium was incorporated into Characae tissues rather than simply complexing on the calcareous surface.

Bacterial influence on arsenic immobilization and remobilization

Laboratory experiments using synthetic mine water containing As (0.2 mg L⁻¹) under defined organic carbon and SO₄²⁻ abundance confirmed the significance of Characea in enhancing As immobilisation. Further, experiments with bacteria extracted from biofilms on the surface of Characea demonstrated enhanced immobilisation of arsenic (Fig. 6). Thus, organic carbon had two roles, namely, the transport of adsorbed As, and stimulating growth of iron and sulphate-reducing bacteria, which

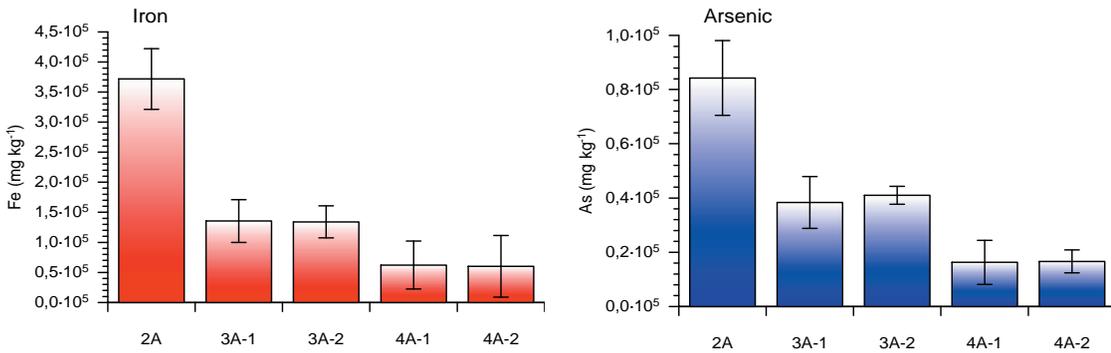


Fig. 3 (left) gradient content of arsenic in sediment collected from sediment traps, and (right) gradient iron content in the sediment collected from the traps

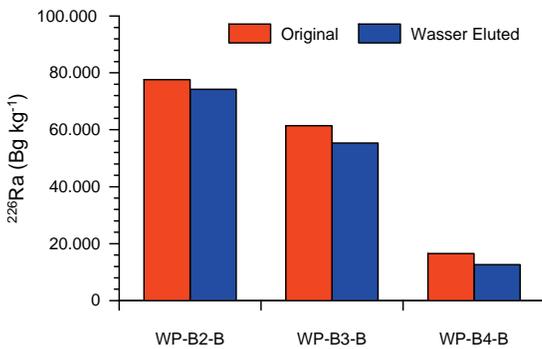


Fig. 4 The fixation of Ra in the sediment from sediment traps in the basin. Analysis was one month after sampling.

in turn promotes As immobilization as As₂S₃ precipitate, accounting for the presence of As(III) in the treatment ponds.

Conclusions

These investigations have provided insights into wetland treatment efficiency as influenced by bacterial activity, material load, remobilization of pollutants and their distribution in the wetland compartments. Competing abiotic and biotic processes limit the efficiency of constructed wetlands in metal removal. Sorption, precipitation and co-precipitation are the principal As-immobilisation processes; bacteria also mediate these processes and play a significant role.

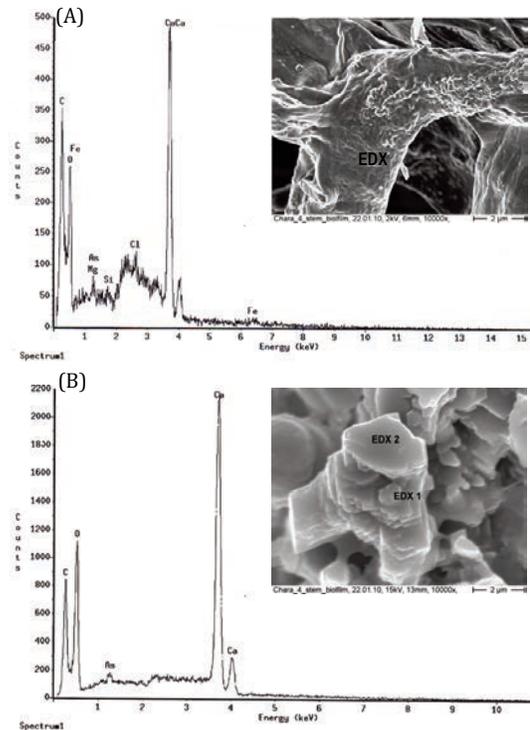


Fig. 4 SEM-EDX characterization of elements on the surface structures of Characea: (a) after careful rinsing with water, (b) after the ultrasonic cleaning (5 minutes). The SEM images show the location of the sample on which the elemental composition was determined by EDX

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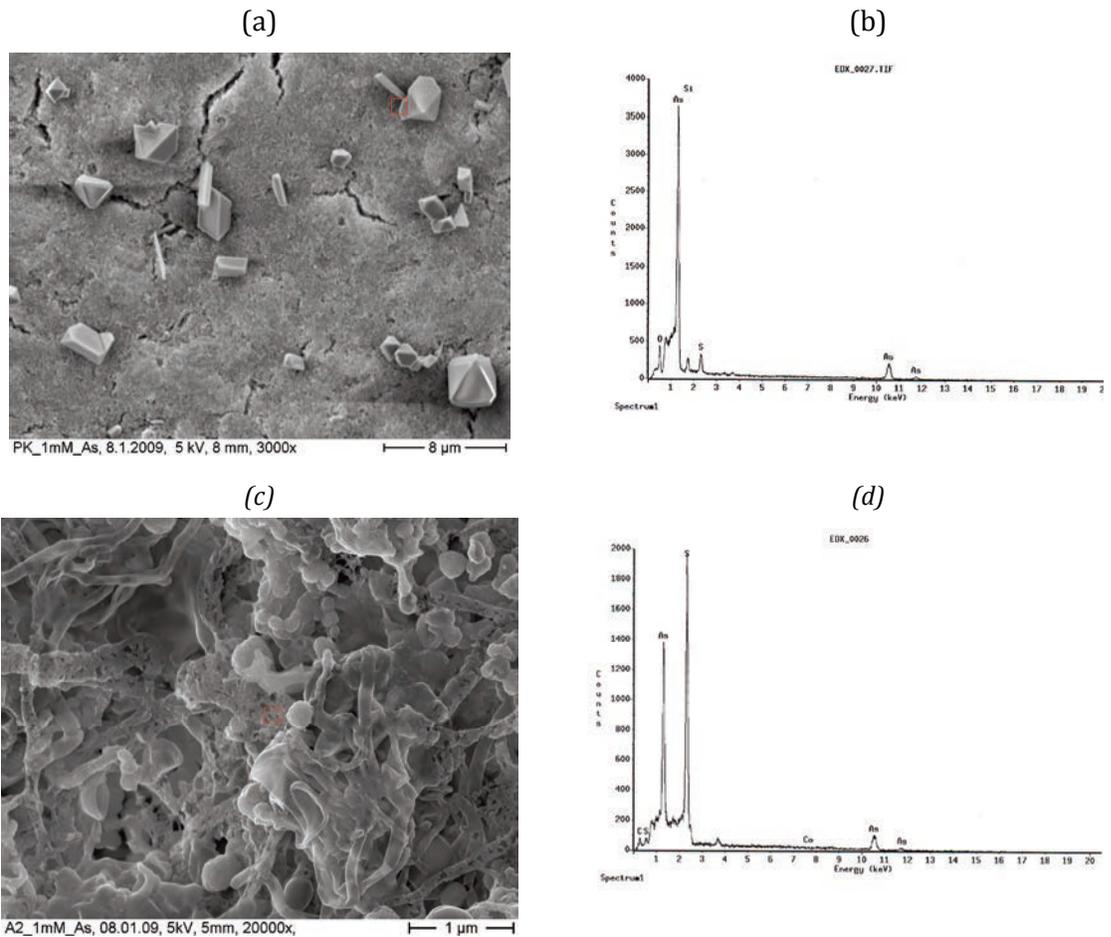


Fig. 5 (a) The crystal structure in some bacterial cultures with 1 μM arsenic, (b) EDX spectrum of the crystallite, (c) the amorphous structure in ordinary bacteria and (d) the EDX spectrum of the amorphous structure

Treatment	Radium (kBq kg ⁻¹)
Control Extraction with dist. H ₂ O	30.1 ± 9.7
Extraction with CH ₃ COOH/CH ₃ COONa; buffered at pH 4.5	27.2 ± 11.2

Table 2 Influence of calcite deposits on Characea surface on radium activity

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References

Dudel GE, Brackhage C, Dienemann H, Mkandawire M, Weiske A (2004) Optimising natural attenuation of trace contaminants from uranium mine tailing waters by nature like constructed wetlands. In: Jarvis

- AP, Dudgeon BA, Younger PL (eds) *Mine Water – Process, Policy and Progress*, vol 2. University of Newcastle upon Tyne Press, Newcastle,
- Eyrolle F, Charmasson S (2001) Distribution of organic carbon, selected stable elements and artificial radionuclides among dissolved, colloidal and particulate phases in the Rhône River (France): Preliminary results. *Journal of Environmental Radioactivity* 55 (2):145-155
- Guo L, Warnken KW, Santschi PH (2007) Retention behavior of dissolved uranium during ultrafiltration: Implications for colloidal U in surface waters. *Marine Chemistry* 107 (2):156-166
- Hallberg KB, Johnson DB (2003) Passive mine water treatment at the former Wheal Jane tin mine, Cornwall: important biogeochemical and microbiological lessons. *Land Contamination & Reclamation* 11 (2):213-220
- Keiper JB, Deonier DL, Jiannino J, Sanford M, Walton WE (2002) Biology, immature stages, and redescription of *Hydrellia personata* Deonier (Diptera : Ephydriidae), a Lemna miner. *Proceedings of the Entomological Society of Washington* 104 (2):458-467
- La Force MJ, Hansel CM, Fendorf S (2000) Constructing simple Wetland Sampling Devices. *Soil Sci Soc Am J* 64:809–811
- Marchand L, Mench M, Jacob DL, Otte ML (2011) Metal and metalloid removal in constructed wetlands, with emphasis on the importance of plants and standardized measurements: A review. *Environmental Pollution* 158:3447–3461
- Woulds C, Ngwenya BT (2004) Geochemical processes governing the performance of a constructed wetland treating acid mine drainage, Central Scotland. *Applied Geochemistry* 19:1773–1783